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# On the twist-bend nematic phase formed directly from the isotropic phase

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The intriguing twist-bend nematic phase ( $N_{TB}$ ) is formed, primarily, by liquid crystal dimers having odd spacers. Typically the phase is preceded by a nematic phase (N) via a weak first-order transition. Our aim is to obtain dimers where the  $N_{TB}$  phase is formed directly from the isotropic phase via a strong first-order phase transition. The analogy between such behaviour and that of the smectic A (SmA)-N-I sequence suggests that this new dimer will require a short spacer. This expectation is consistent with the prediction of a molecular field theory since the decrease in the spacer length results in an increase in the molecular curvature. A vector of odd dimers based on benzyloxybenzylidene mesogenic groups with terminal ethoxy groups has been synthesised with spacers composed of odd numbers of methylene groups. Spacers having 5, 7, 9, and 11 methylene groups are found to possess the conventional phase sequence  $N_{TB}$ -N-I; surprisingly for the propane spacer the  $N_{TB}$  phase is formed directly from the isotropic phase. The properties of these dimers have been studied with care to ensure that the identification of the  $N_{TB}$  phase is reliable.

**Keywords:** twist-bend nematic, helicoidal structure,  $N_{TB}$ -N,  $N_{TB}$ -I, first-order phase transitions, rope-like optical texture, liquid crystal dimers, benzyloxybenzylidene mesogen,  $^2H$  NMR spectroscopy, prochiral splitting, molecular field theory

## 1. Introduction

In 1888 Reinitzer reported the synthesis of cholesteryl benzoate with its unusual double melting and striking colours seen on cooling the compound to just above the freezing point [1]. It was then found that this and similar compounds exhibited the cholesteric phase, now known as the chiral nematic phase and, as this name suggests, at the local molecular level the nematic and chiral nematic phases are similar [2]. The key difference at the macroscopic

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level is that the director is twisted into a helical structure with the helix axis orthogonal to the director [3]. The driving force for the formation of the chiral nematic phase is the chirality of the constituent molecules. Much later, in 2001, Dozov predicted the existence of a more general chiral nematic phase known as the twist-bend nematic ( $N_{TB}$ ) [4]; in its helicoidal structure the director is tilted with respect to the helix axis and so the chiral nematic is a special case of it. More strikingly this chiral phase is formed by molecules which are not, in themselves, chiral and it is the bent shape of the constituent molecules which provides the driving force for its formation possibly as a result of the negative value of the bend elastic constant [5]. An alternative explanation for the existence of the  $N_{TB}$  phase, although forgotten for many years, was given by Meyer [6] who predicted that the polarity of a nematic phase would lead to a twist-bend structure.

Ten years after its prediction by Dozov [4] Cestari et al. [7] reported a detailed investigation of the liquid crystal dimer 1'',7''-bis(4-cyanobiphenyl-4'-yl) heptane (CB7CB), with its odd spacer length, which exhibited two nematic phases that at the lower temperature being the  $N_{TB}$  phase. This result has been confirmed by other studies some of which showed that the pitch of the helix is remarkably short, typically of the length of several molecules [8-11]. The original Landau-like theory [4] predicts that the  $N_{TB}$ –N transition is second order, a result consistent with that of a novel molecular field theory [12]. These predictions contrast with the behaviour of CB7CB where the  $N_{TB}$ –N transition is found to be first order [7]. Indeed studies of other analogous odd liquid crystal dimers [13] and their mixtures [14] confirm this result; it is also observed that as the nematic range increases so the strength of the  $N_{TB}$ –N transition decreases [15]. Such behaviour is analogous to that of compounds exhibiting both nematic and smectic A phases [16]; this is not surprising given the formal similarity between the  $N_{TB}$  and smectic A phases [4,17]. This analogy would also suggest that the twist-bend nematic phase might also be formed directly from the isotropic phase via a first-order transition.

Indeed the molecular field theory [12] based on symmetric V-shaped molecules also predicts this first order  $N_{TB}$ –I transition when the angle between the mesogenic arms, has fallen from  $140^\circ$  to  $130^\circ$ . This reduction in the interarm angle would also be consistent with the decrease in the length the spacer linking the two mesogenic groups. Here we report our successful search for a liquid crystal dimer exhibiting a twist-bend nematic-isotropic transition which will, we expect, stimulate the development of the theoretical models for the  $N_{TB}$  phase [4,18,19].

Our starting point is the previous observation that to create the first-order  $N_{TB}$  - I phase transition the spacer length should be reduced. We require, therefore, a homologous series of liquid crystal dimers where we can vary the length of the flexible spacer between the mesogenic groups. The dimers that we have chosen are the  $N,N'$ -bis[4'-(4"-alkyloxybenzoyloxy)benzylidene]alkane- $\alpha,\omega$ -diamines with odd spacer lengths (see Scheme1). These compounds are denoted by the mnemonic  $mO.n.Om$  where  $n$  is the number of methylene groups in the spacer and  $m$  is the number of carbon atoms in a terminal alkyloxy group. Such dimers have been studied by Šepelj et al. [20] who found that the odd dimer 4O.7.O4 exhibited a nematic-nematic phase transition but did not identify the low-temperature nematic phase and so labelled it as  $N_x$ . With hindsight it is now clear that this dimer, with the methylene links between the odd spacer and the mesogenic groups, forms a twist-bend nematic phase. Given this structural element and the additional feature of the terminal alkyloxy chains it seems that would be reasonable to explore the odd dimers  $mO.n.Om$  in our search for the  $N_{TB}$  - I phase transition. We have prepared 30 members of this matrix but here we shall be concerned with just five dimers of the vector 2O. $n$ .O2 where  $n$  takes odd values from 3 to 11.

In the following Section we shall describe the synthesis of these dimers and the techniques used to identify the products as well as to characterise the mesophases that they form; clearly

an important task. In Section 3 the transitional properties of the five dimers are listed. These are followed by the properties of the mesophases exhibited by, amongst others, the dimer 2O.9.O2 and employed to identify them. Our conclusions are given in Section 4.

## **2. Experimental**

### **2.1 Synthesis**

The dimers 2O.*n*.O2 were synthesised according to the route given by Šepel et al. [20] and shown in Scheme 1. All of the starting materials were obtained commercially (Aldrich UK). The benzoate esters were prepared using the procedure described by Thaker et al. [21]; the yields for these were typically good being of the order of 75%. The Schiff base dimers were prepared under dry nitrogen to inhibit decomposition of the products; similar precautions were taken in their investigation. They were recrystallized twice from dry ethanol and the white powders dried in a vacuum; the yields were typically about 60%. The products were routinely characterised using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, IR spectroscopy and electrospray mass spectroscopy. The purity of the products was demonstrated using elemental analysis.

### **2.2 Mesophase Characterisation**

The phase behaviour of the five odd dimers 2O.*n*.O2 with *n* = 3-11 was characterised with (i) polarising optical microscopy (Weiss polarising microscope together with a Linkam TP 94 hotstage and temperature controller); (ii) differential scanning calorimetry (DSC) (Universal V4.5A TA model DSC Q1000); (iii) X-ray scattering (Ganesha 300 XL apparatus; Genix 3D source with copper K $\alpha$  radiation (1.54Å) and a Pilatus 300k detector with the sample and detector kept under vacuum. An electromagnet with a maximum field of 1T was available to align the sample. This was heated with a bespoke heater and a Eurotherm 818P controller) and (iv) <sup>2</sup>H NMR spectroscopy (Two spectrometers were used. (1) A 400MHz Bruker AVII

spectrometer using a single pulse sequence with a magnetic field of 9.40 T. This high field is, necessarily, also used to align the nematic phases. The sample temperature was calibrated from the  $^1\text{H}$  NMR spectrum of ethylene glycol dissolved in  $\text{DMSO-d}_6$ . (2) This was a Varian Chemagnetics CMX Infinity spectrometer which also has a magnetic field strength of 9.40 T. The sample temperature was controlled with a Chemagnetics temperature unit it is stable to  $\pm 0.5^\circ\text{C}$ . The spectra were measured with a single pulse sequence with a pulse width of  $5\mu\text{s}$  and the relaxation delay between the end of the acquisition of the FID and the pulse was 0.05s.)

### 3. Results and Discussion

All of the five odd dimers have been characterised in essentially the same way employing the same techniques. We shall start by discussing the results for the dimer 2O.9.O2 as an exemplar of the series. As we shall see this dimer forms an enantiotropic phase sequence  $\text{Cr} - \text{N}_{\text{TB}} - \text{N} - \text{I}$ ; the transition temperatures and the dimensionless transitional entropies,  $\Delta S/R$ , are shown in Table 1; the transition temperatures are also shown in Fig. 1. We shall return to all of these shortly. The nematic phase was identified from its fluidity and by the marble texture shown in Fig. 2(a). The texture observed on lowering the temperature to the twist-bend nematic phase is given in Fig. 2(b) and is a mixture of a polygonal together with a rope-like form. This is often observed for the  $\text{N}_{\text{TB}}$  phase and is related to a periodic form resulting from the helicoidal structure with its short pitch [7, 20].

Further support of these assignments for 2O.9.O2 is provided by the four X-ray scattering patterns which are shown in Fig. 3. In Fig. 3(a) the dimer at  $110^\circ\text{C}$  has the highly structured circular pattern showing that the sample is clearly in the unaligned crystal phase. To prepare the dimer in the two nematic phases it was first heated into the isotropic phase whose scattering pattern in Fig. 3(b) contains two diffuse circles. One is the wide-angle circle

corresponding to side-by-side correlations with a local distance of  $4.6\text{\AA}$  which is also typical of rod-like molecules. The other is the small-angle scattering circle which corresponds to a repeat length of about  $19.2\text{\AA}$  along the director. The molecular length of 2O.9O2 in its elongated form is estimated from Hyperchem to be  $37.2\text{\AA}$ , essentially twice the repeat length which corresponds to a locally intercalated structure [23, 24]. On passing to the nematic phase in the presence of a 1T magnetic field the wide and small-angle circles are transformed into arcs showing that the director is aligned parallel to the magnetic field (See Fig. (3c)). The small-angle arcs are diffuse which reveals that there is no long-range translational order so that the phase is certainly nematic and not smectic. The wide-angle arc is clearly pronounced and if the director is well aligned could be used to estimate the orientational distribution function although for which intermolecular axis is not clear given the bent form of the molecule. On passing from the N to the  $N_{TB}$  phase the radial extent of the small-angle arcs is slightly increased in extent (See Fig. (3d)); this is consistent with the lack of long-range translational order showing that this phase is not a smectic and has a structure consistent with the  $N_{TB}$  phase. It is also interesting that in the twist-bend nematic phase the azimuthal extent of the wide-angle arcs is slightly larger than in the nematic phase. The same difference between the wide-angle arcs of the N and  $N_{TB}$  phases is also observed for the liquid crystal dimer CB9CB [25]. Perhaps of greater interest is the observation for the  $N_{TB}$  phase of 2O.9O2 that the extent of the arcs becomes larger as the temperature is lowered further. There are several possible reasons for this including the increase in the director tilt. The small-angle arc shifts very slightly in the  $N_{TB}$  phase for 2O.9O2 and so gives a repeat length of  $18.4$  to  $17.3\text{\AA}$  but the ratio of the local end-to-end repeat length to that of the molecule remains at about 0.5. The local intercalated structure although seen for other phases does appear to be a recurring feature for the twist-bend nematic phase perhaps associated with the packing of molecules having an averaged local V-shape.

The final technique used here to characterise the  $N_{TB}$  phase is  $^2H$  NMR spectroscopy. This has proved to be a powerful approach for investigating liquid crystals, for example, by determining their defining, long-range orientational order [26]. Subsequently it has been shown to be capable of demonstrating the form chirality of the twist-bend nematic phase constituted as it is from achiral molecules [7]. This application has been built on the use of NMR spectroscopy to investigate enantiomeric forms of non-mesogens with chiral nematic hosts [27]. For the  $N_{TB}$  phase we require achiral molecules containing prochiral groups, such as a methylene group. In an achiral host the two deuterons are equivalent because of the local plane of symmetry in this group but the equivalence is lost when the host is chiral. To exploit this feature since the 2O.*n*.O2 dimer is not deuteriated we have added a small amount of the analogous dimer CB7CB- $d_4$  in which the methylene groups at positions 1'' and 7'' of the heptane spacer had been specifically deuteriated [7]. In the N phase of 2O.9.O2 at 105.7°C the deuterium NMR spectrum of the probe contains a single quadrupolar doublet, shown in Fig. 4(a), which results from the equivalence of the two methylene groups and the mirror symmetry between the deuterons in individual groups [28]. On lowering the temperature into the  $N_{TB}$  phase at 99.9°C and 84.1°C the resultant chiral phase with its global  $D_\infty$  symmetry causes the methylene groups to lose their planes of symmetry and the deuterons to lose their equivalence. This loss results in the appearance of the two quadrupolar doublets seen in Figs. 4(b) and 4(c); it provides striking evidence for the chirality of the  $N_{TB}$  phase and the identification of the twist- bend nematic phase formed by the dimer 2O.9.O2.

The  $^2H$  NMR experiments give not only qualitative information as to whether a mesophase is chiral or not, they also give some qualitative information on the nature of the phase transition as well as the structure of the phases either side of this. This is achieved by examining the variation of the quadrupolar splittings,  $\Delta\nu$ , with temperature through the two phases. The results for CB7CB- $d_4$  doped in 2O.9.O2 are shown in Fig. 5 as a function of the shifted



temperature ( $T_{NI} - T$ ). In the N phase there is just a single quadrupolar splitting and its magnitude grows as the shifted temperature increases. However, as the  $N_{TB}$  phase is approached so the rate of increase in  $\Delta\nu$  decreases and a plateau is clearly reached. This is in marked contrast with the behaviour of CB7CB- $d_4$  where the quadrupolar splitting grows rapidly even as the  $N_{TB}$ -N transition is reached. This difference is consistent with the significant change in the nematic range which is  $\sim 25^\circ\text{C}$  for 2O.9.O2 and just  $\sim 13^\circ\text{C}$  for CB7CB [7]. It is also in agreement with the correlation between the nematic range and the transitional entropy,  $\Delta S_{N_{TB}N}/R$ , this is  $\sim 0.20$  for the former dimer and  $\sim 0.31$  for the latter. As we have noted this dependence of the transitional entropy on the nematic range is analogous to that of a SmA-N system [4,17]. We now see that the temperature dependence of the quadrupolar splitting and variation with the nematic range is, to a certain extent, consistent with that predicted for the SmA-N system [16].

In the  $N_{TB}$  phase the spectrum contains two quadrupolar splittings associated with their loss of equivalence resulting from the chirality of the phase. These two splittings, shown in Fig. 5 as enclosed blue squares, can be written in terms of their mean which is related to the orientational order of the phase and is comparable with the splitting observed in the nematic phase. The mean is shown as green diamonds and is essentially continuous with the splitting in the nematic phase which is consistent with the weakness of the  $N_{TB}$ -N transition. The mean splitting increases very slowly with increasing shifted temperature which results from the balance between the increasing orientational order and the conical angle also increasing; the former causes the quadrupolar splitting to increase and the latter causes it to decrease [28, 29]. The difference in the two splittings results from the chirality of the  $N_{TB}$  phase [28] and so is called the chiral splitting; on entering the phase this splitting is essentially zero again consistent with the weak transition. As the shifted temperature,  $(T_{N_{TB}N} - T)$ , increases from  $0^\circ\text{C}$  so the chiral splitting grows and reaches its largest value of  $\sim 13$  kHz when the shifted

temperature is 30°C. It is interesting to compare these results with those for CB7CB-d<sub>4</sub> which is one of the most studied liquid crystal dimers exhibiting the twist-bend nematic phase. When the shifted temperature is zero the chiral splitting is ~3 kHz, in keeping with the stronger first-order phase transition. At a shifted temperature of 30°C for CB7CB-d<sub>4</sub> the chiral splitting is ~15 kHz [7]. This final value is similar to that for the dimer 2O.9.O2 especially if allowance is made for the chiral splitting at the N<sub>TB</sub>-N transition. The similarity in behaviour for the two dimers given their quite different structures, which may hint at a universality in behaviour, is perhaps surprising and remains to be understood completely.

Consideration of the detailed results for the characterisation of 2O.9.O2 and indeed the other dimers reveals that the three dimers with  $n$  equal to 7, 9, and 11 have a common phase sequence, Cr – N<sub>TB</sub> – N – I, here the phase transitions are all enantiotropic. In addition the first-order N<sub>TB</sub> – N transition increases in strength as  $n$  decreases together with the length of the nematic phase. When  $n$  reaches 5 the transitions are monotropic but it is possible to supercool the phases of this dimer. This shows that 2O.5.O2 still forms the two nematic phases N<sub>TB</sub> and N although as expected the nematic range has decreased. Given the size of the relative reductions in the nematic range it might seem unlikely that the next homologue 2O.3.O2 would exhibit the sought-after N<sub>TB</sub>–I transition, In addition the freezing point of this dimer shown in Fig.1 is significantly greater than the previous homologue and so we did not expect to find any liquid crystal phases. However, after considerable efforts and patience it did, eventually, prove possible to supercool a sample of 2O.3.O2 sufficiently under the polarising microscope to observe the texture of just one monotropic mesophase and this is shown at approximately 87°C in Fig. 6. This texture is clearly not of a nematic phase but has rope-like and polygonal features typical of the twist-bend nematic phase. Our success with this encouraged us to use DSC to locate the N<sub>TB</sub>–I transition and also to determine the transitional entropy. We find T<sub>N<sub>TB</sub>I</sub> to be 87.4°C which requires the isotropic phase to have

been supercooled by 56.4°C before the  $N_{TB}$  phase is reached, this experiment then gives  $\Delta S_{N_{TB}I}/R$  as  $\sim 0.74$  indicating a fairly strong first-order phase transition. The appearance of this transition clearly shows that the extent to which this dimer is bent is proportionally greater than for its higher homologue with  $n$  equal to 5. In such studies we always endeavour to provide strong evidence for the identification of the twist-bend nematic phase. We have, therefore, attempted to obtain X-ray scattering patterns and  $^2H$  NMR spectra of CB7CB- $d_4$  doped in 2O.3.O2 but this requires bulk samples which tended to crystallise before the  $N_{TB}$  phase is formed and so these experiments were not possible.

It has been necessary, therefore, to attempt a different approach with which to stabilise the  $N_{TB}$  phase and to lower the freezing point. Surprisingly it proved possible to do this by making a binary mixture of 2O.3.O2 with its higher homologue 2O.5.O2. The phase diagram for the mixture, determined with optical microscopy, is shown in Fig. 7. What we see is that the N-I transition temperature of 2O.5.O2 is lowered by the addition of 2O.3.O2 until the mole fraction of this component is  $\sim 0.4$ . At this point the isotropic phase passes directly to the twist-bend nematic phase. We see that the  $N_{TB}$ -N transition line is continuous with the  $N_{TB}$ -I line in the remainder of the phase diagram which provides further evidence for the identity of the twist-bend nematic phase formed by 2O.3.O2. It was also possible to determine the transitional entropies across the entire phase diagram and these are shown in Fig.8. They indicate that  $\Delta S_{NI}/R$  is more or less constant at about 0.08 and this small value is consistent with the bent average form of the dimers. More strikingly  $\Delta S_{N_{TB}N}/R$  increases significantly with the concentration of 2O.3.O2 consistent with its high average bent structure; this growth increases at a slightly higher rate once the twist-bend nematic phase appears directly from the isotropic phase with results consistent with the transitional entropy of  $\sim 0.74$  measured directly for 2O.3.O2. Such a change with the increasing concentration of 2O.3.O2

is analogous to that predicted for the SmA-N and SmA-I caused by an increase in the smectic driving force [16].

Given this ability to supercool the mixture past the  $N_{TB}$ -I transition we have used an equimolar mixture of the two dimers to determine both the X-ray scattering patterns and the  $^2H$  NMR spectra. The scattering patterns are shown in Fig. 9 and at 124°C in (a) the sample is in the isotropic phase which gives some indication of how the melting point has been reduced in the mixture. The pattern consists of two broad circles, small angle and wide angle. The sample temperature was then reduced to 86°C which is in the  $N_{TB}$  phase while applying a magnetic field of 1T. The result scattering pattern in Fig. 9(b) is essentially unchanged to that in the isotropic phase of Fig. 9(a); this shows that the field of 1T is unable to align the  $N_{TB}$  phase either directly or by cooling from the isotropic phase. This contrasts with the behaviour for the dimer 2O.9.O2 shown in Fig. 3 where the  $N_{TB}$  phase is aligned by the same field but this occurs because the magnetic field first aligns the director in the nematic phase and from this the helix axis of the  $N_{TB}$  phase is aligned. The repeat length along the helix axis does not appear to change between the two phases and that a locally intercalated structure occurs in both, essentially as found for the single component dimers.

The  $^2H$  NMR spectra of CB7CB- $d_4$  doped in the equimolar mixture were also measured using the Varian Chemagnetics spectrometer. This has a large magnetic field of 9.40T which is able to align the helix axis of the  $N_{TB}$  phase directly as is apparent from the narrow lines of the quadrupolar doublets shown in Fig. 10. At 91°C the sample is in the isotropic phase as is apparent from the single albeit broad peak. On lowering the temperature to 89°C the single peak broadens consistent with the high viscosity of the dimer host. In addition it is joined by two quadrupolar doublets clearly showing the chirality of the nematic phase and its identity as a twist-bend nematic phase. This biphasic region where the  $N_{TB}$  and I phases co-exist over a narrow temperature range demonstrate quite clearly the first-order nature of the transition.

Just 1°C at 88°C the isotropic peak has vanished and we see that the peaks have sharpened and grown in intensity enlarged quadrupolar splittings. This process continues as the temperature is lowered and the spectral baseline improves. The quadrupolar splittings obtained from the spectra for CB7CB-d<sub>4</sub> are shown in Fig. 11 plotted as a function of the shifted temperature,  $T_{\text{NtBI}} - T$ . We see that at the phase transition there is a relatively large chiral splitting of 7.95 kHz consistent with the large transitional entropy. As the shifted temperature increases so the chiral splitting also grows until at the largest shifted temperature of 25°C the chiral splitting has reached 12.5 kHz. This is essentially the same as that found for CB7CB-d<sub>4</sub> in the pure dimer 2O.9.O2 although here the chiral splitting is essentially zero at the N<sub>TB</sub> -N transition. Clearly we need to work further on our new systems to understand these intriguing results.

#### 4. Conclusions

Guided in our search for a mesogen exhibiting the N<sub>TB</sub>-I transition by pragmatism and theory we have looked for an odd liquid crystal dimer with benzoyloxybenzylidene mesogenic groups having a short spacer by extrapolating from those with longer spacers. Eventually, with patience we found that 2O.3.O2 did indeed form the twist-bend nematic phase directly from the isotropic phase having the expected large transitional entropy,  $\Delta_{\text{NtBI}}/R$ , of ~0.74. This was only achieved by cooling the isotropic phase extensively below the freezing point which appeared too large to make extensive studies on the macroscopic N<sub>TB</sub> phase. However, we were able to stabilise this phase by mixing the dimer with its higher homologue 2O.5.O2. The equimolar mixture which exhibits the N<sub>TB</sub> - I transition allowed us to characterise the twist-bend phase by using X-ray scattering after its formation from the isotropic phase. More importantly it was also possible to use <sup>2</sup>H NMR to explore the chirality and orientational order of the novel phase. These are, as might be expected, high in comparison with those of the N<sub>TB</sub> formed from the N phase exhibited by analogous dimers and await more detailed

analysis. Finally the existence of the  $N_{TB} - I$  phase transition is in good accord with the molecular field model based on a V-shaped molecule and demonstrates the importance of this [12]. It now remains to be seen to what extent other models of the twist-bend nematic phase [4,18,19] can predict its transition direct to the isotropic phase and the variation of this phase transition with the molecular structure.

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### **Addendum**

After our paper was complete we learnt of a study of the phase behaviour of a dimer with a nonane spacer doped with a novel, highly chiral compound where the direct transition of an isotropic phase to the twist-bend phase had also been reported [31].

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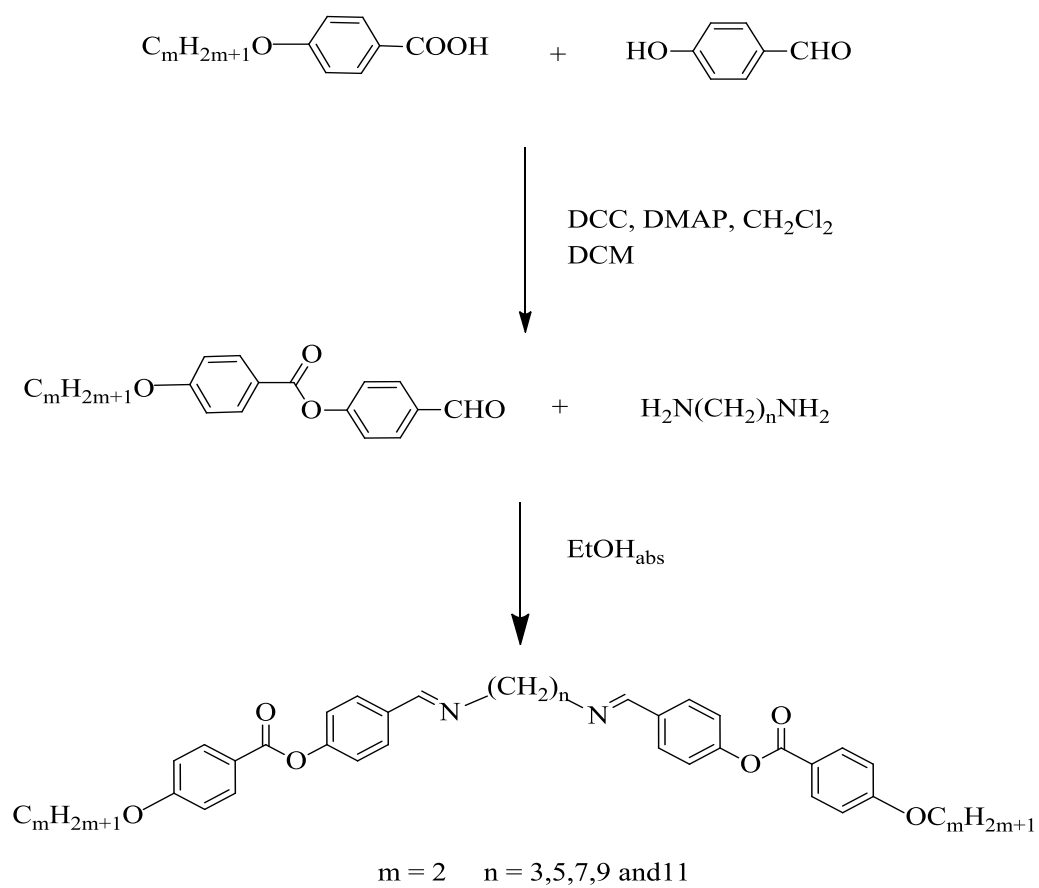
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## Figures



Scheme 1. Synthetic route to the liquid crystal dimers  $m\text{O}.n.\text{Om}$  for  $m = 2$  and  $n = 3, 5, 7, 9, 11$ .

Table 1. The transition temperatures ( $^{\circ}\text{C}$ ) and transitional entropies ( $\Delta S/R$ ) shown in square brackets for the odd liquid crystal dimers  $2\text{O}.n.\text{O}2$  with  $n = 3, 5, 7, 9$ , and  $11$ . Round brackets indicate a monotropic transition.

Dimer	$*T_{\text{CrI}}$ $T_{\text{CrNtb}}$	$T_{\text{Ntbl}}$	$T_{\text{NtbN}}$	$T_{\text{NI}}$	$\frac{\Delta S_{\text{CrI}}/R^*}{\Delta S_{\text{CrNtb}}/R}$	$\Delta S_{\text{Ntbl}}/R$	$\Delta S_{\text{NtbN}}/R$	$\Delta S_{\text{NI}}/R$
2O.3.O2	*143.8	(87.4)	-	-	*[23.73]	[0.74]	-	-
2O.5.O2	*119.0	-	(93.9)	(112.3)	*[15.16]	-	[0.13]	[0.06]
2O.7.O2	95.2	-	104.3	128.4	[12.56]	-	[0.12]	[0.11]
2O.9.O2	93.2	-	102.6	131.3	[14.41]	-	[0.20]	[0.36]
2O.11.O2	96.0	-	103.4	131.6	[15.72]	-	[0.02]	[0.38]

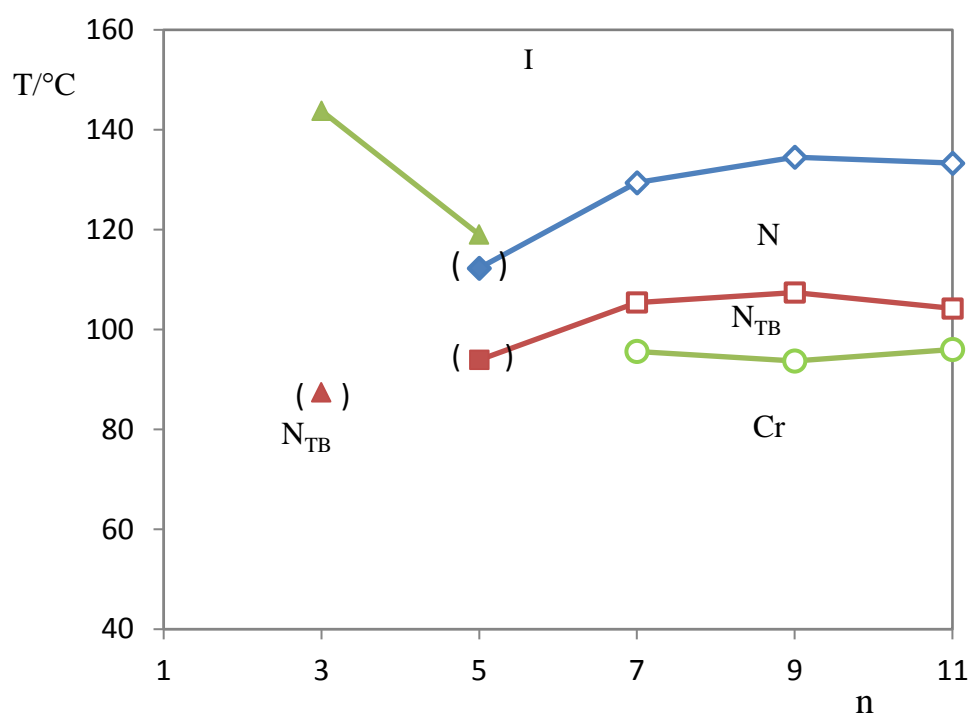
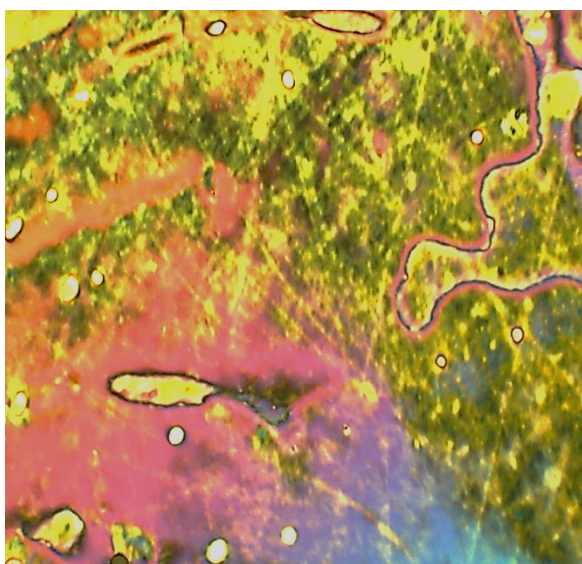


Figure 1. The dependence of the transition temperatures, for both enantiotropic and monotropic transitions, on the length,  $n$ , of the spacer for the liquid crystal dimer, 2O. $n$ .O2.  $\blacktriangle$  denotes the Cr-I transition,  $\circ$  the Cr-N<sub>TB</sub> transition,  $\square$  the N<sub>TB</sub>-N transition, and  $\diamond$  denotes the N-I transition.  $(\blacksquare)$  denotes the (N<sub>TB</sub>-N) transition,  $(\blacklozenge)$  the (N-I) transition and  $(\blacktriangle)$  denotes the (N<sub>TB</sub>-I) transition. Here the round brackets indicate a monotropic transition.

(a)



(b)

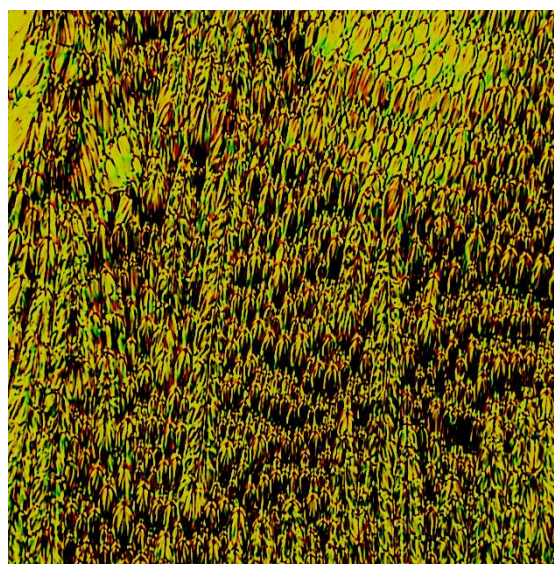


Figure 2. The optical textures of 2O.9.O2 showing (a) the marble texture of the nematic phase at 129.5°C and (b) the polygonal and rope-like texture of the twist-bend nematic phase at 88.2°C. The sample was contained between untreated glass plates.

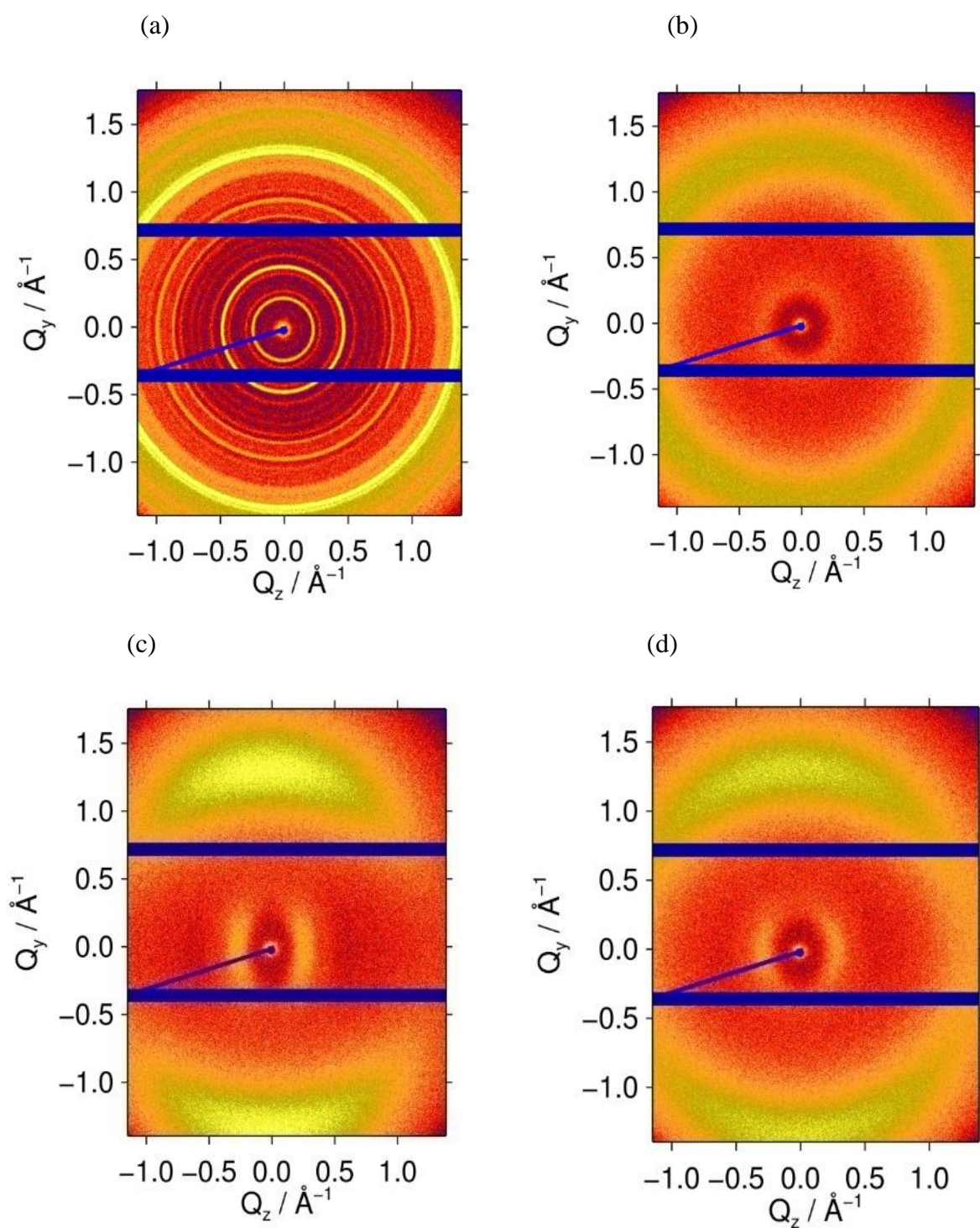


Figure 3. The X-ray scattering patterns of the liquid crystal dimer, 2O.9.O2, in (a) the crystal phase at 100°C, (b) the isotropic phase at 132°C, (c) the nematic phase aligned by a magnetic field of 1T at 110°C and (d) the twist-bend nematic phase at 105°C aligned by cooling in a 1T magnetic field. The sample, typically 25mg, was contained in a 1.5 mm quartz Lindemann tube which was evacuated, filled with argon and sealed with the glue, Araldite.

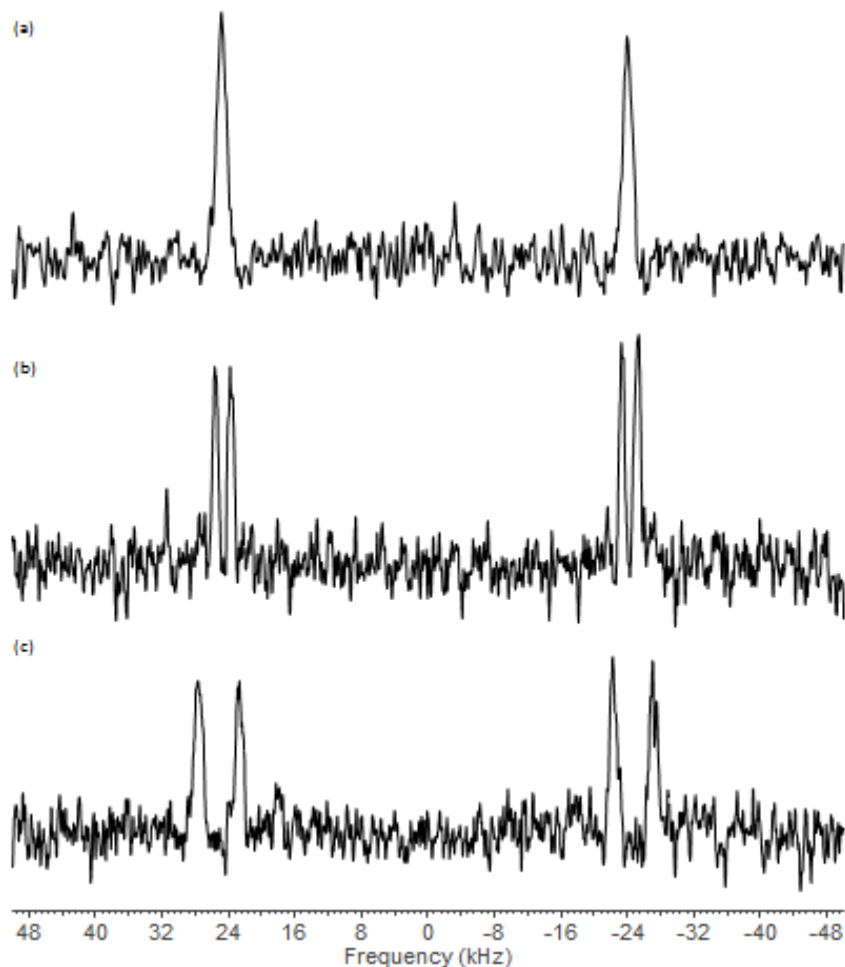


Figure 4. The  $^2\text{H}$  NMR spectra of the probe dimer CB7CB- $\text{d}_4$  doped (2.5wt%) in the analogous dimer 2O.9.O2 in (a) the nematic phase at 105.7°C, (b) the twist-bend nematic phase at 99.9°C and (c) the twist-bend nematic phase at 84.1°C. The sample was contained in a standard NMR tube which was sealed when the sample had been degassed after having been subject to several freeze-thaw cycles. Single pulse sequence with an 18.3 $\mu\text{s}$  of 25W with a pulse delay of 50ms was used; 6k dummy scans prior to acquisition to allow for thermal equilibrium followed by collection of 12k scans.

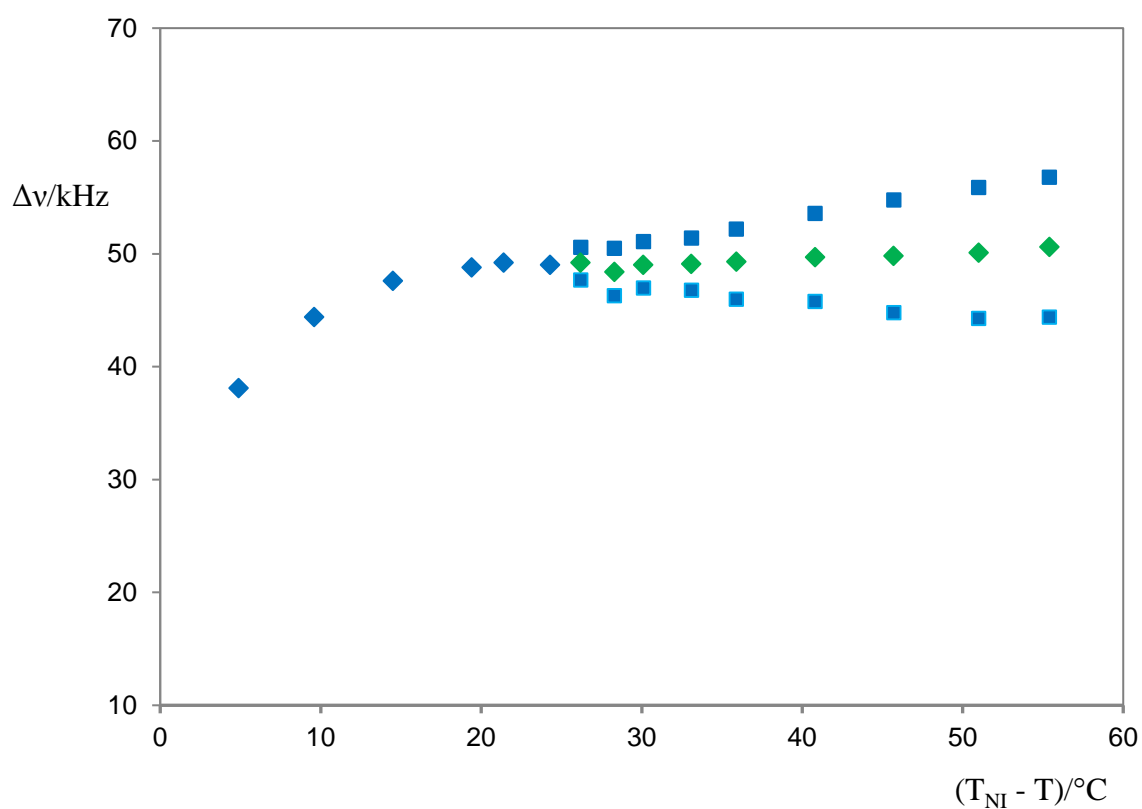


Figure 5. The dependence, on the shifted temperature,  $(T_{NI} - T)$ , of the quadrupolar splittings,  $\Delta v$ , for the spin probe, CB7CB-d<sub>4</sub>, doped (2.5wt%) in the liquid crystal dimer 2O.9.O2. Here  $\blacklozenge$  denotes the quadrupolar splittings in the nematic phase,  $\blacksquare$  the two prochiral splittings in the N<sub>TB</sub> phase and  $\blacklozenge$  the mean of the two splittings, also in the N<sub>TB</sub> phase.



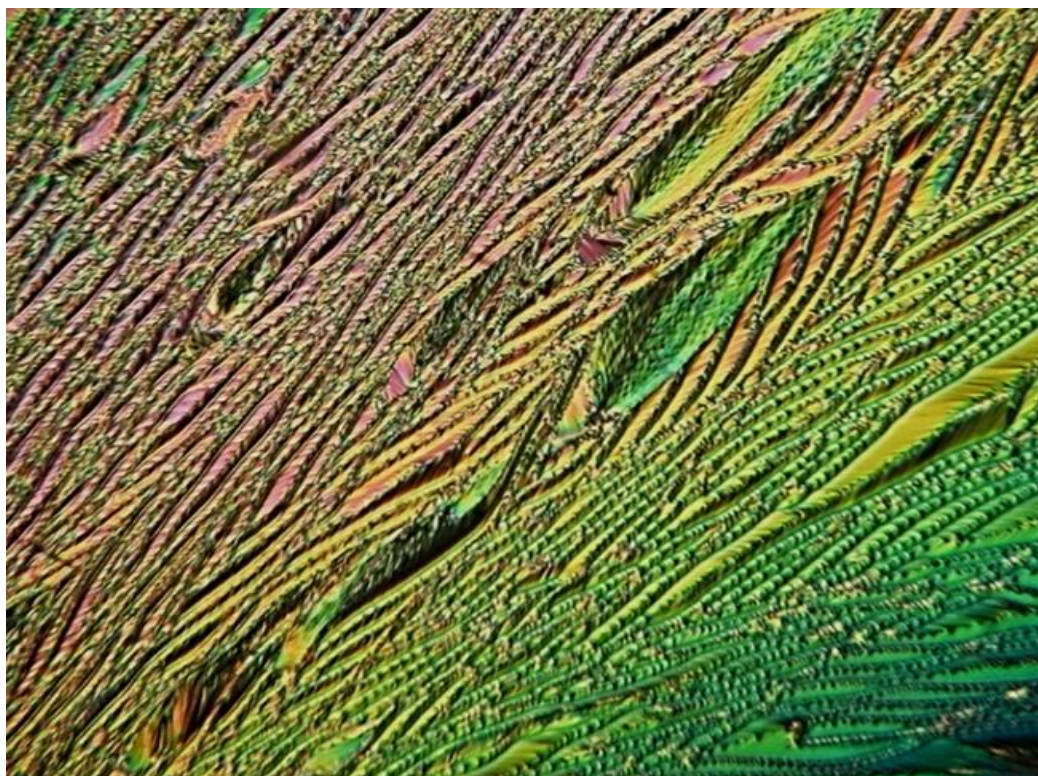


Figure 6. The optical texture of 2O.3.O2 supercooled from the isotropic phase into the twist-bend nematic phase at about 87°C showing a typical rope-like texture. The sample was contained between thin and untreated glass slides.

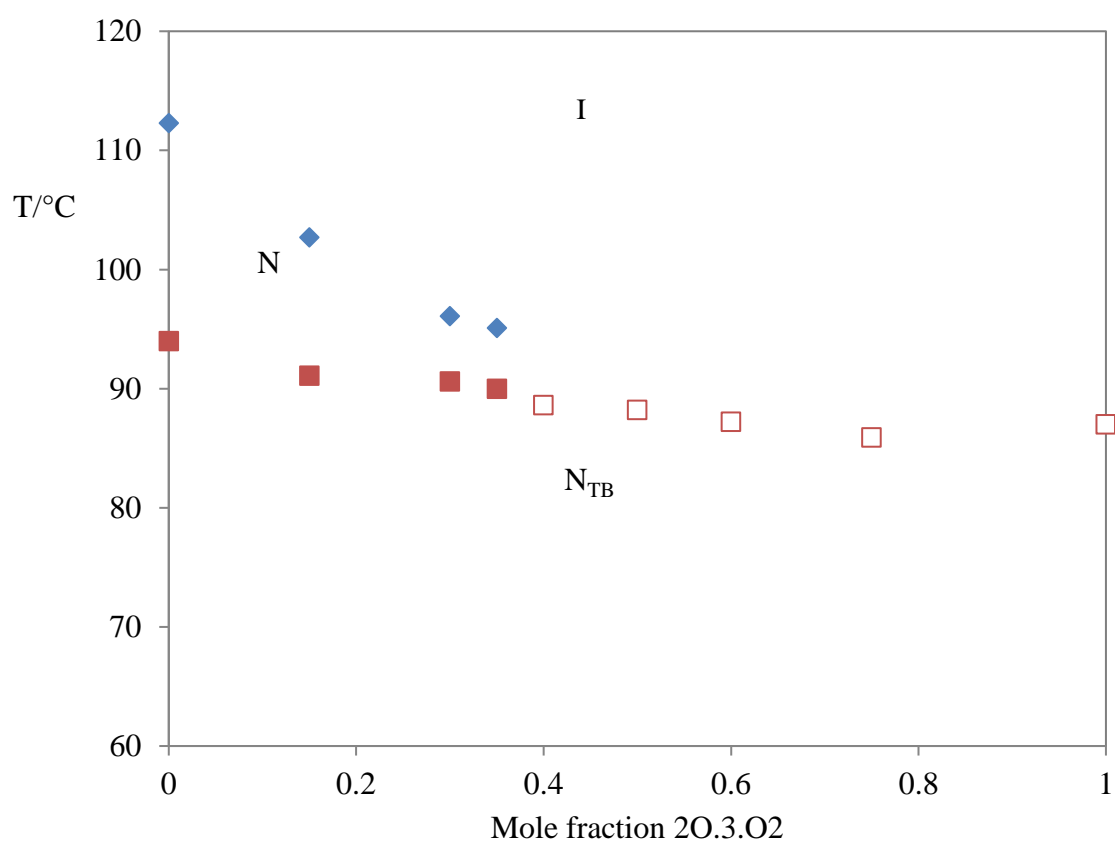


Figure 7. The binary phase diagram for the two homologous liquid crystal dimers 2O.3.O2 and 2O.5.O2. The transitions are monotropic;  $\blacklozenge$  denotes the (N-I) transition,  $\blacksquare$  the ( $N_{TB}$ -N) transition and  $\square$  the ( $N_{TB}$ -I) transition.

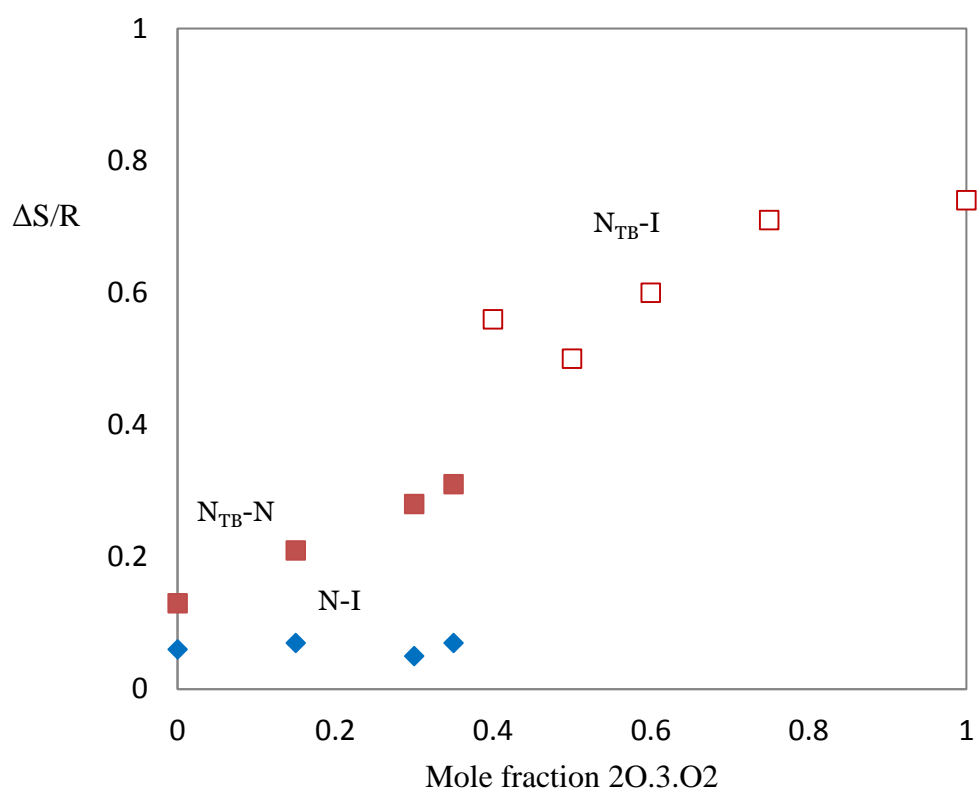


Figure 8. The variation with composition of the transitional entropies,  $\Delta S/R$ , for the binary mixture, 2O.3.O2 and 2O.5.O2, where  $\blacklozenge$  denotes the N-I transition,  $\blacksquare$  the N\_TB-N transition, and  $\square$  the N\_TB-I transition.

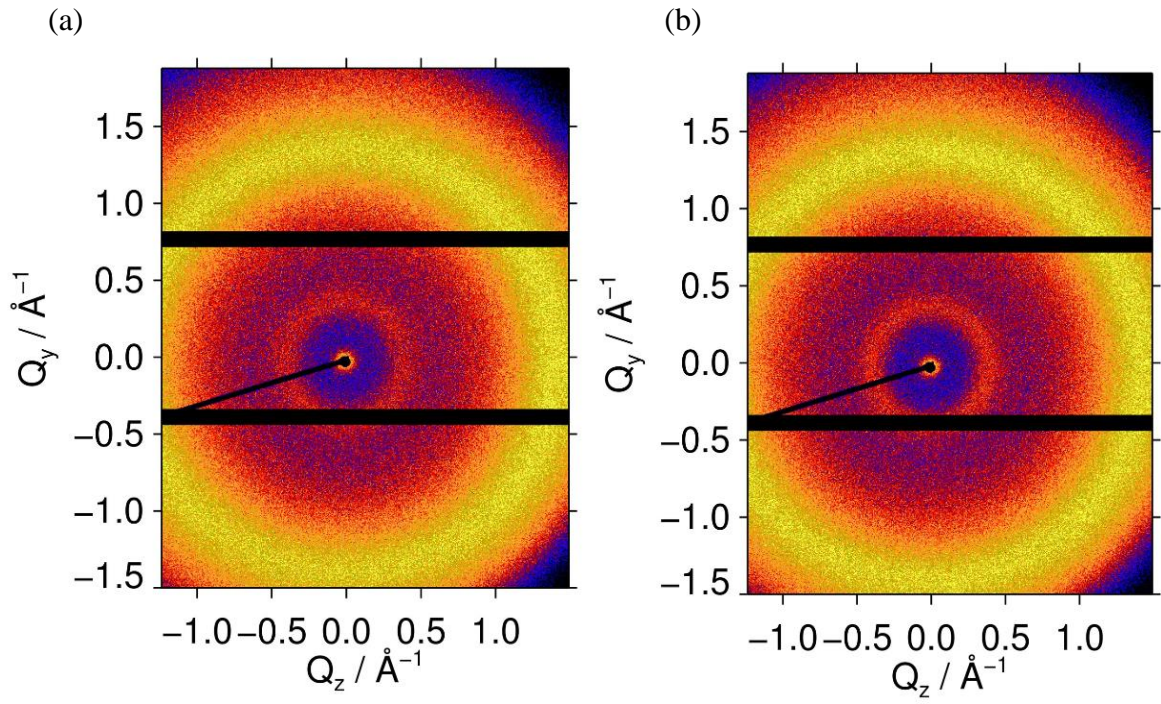


Figure 9. The X-ray diffraction patterns of an equimolar mixture of 2O.3.O2 and 2O.5.O2 in (a) the isotropic phase at 124°C and (b) in the twist-bend nematic phase at 86°C in the presence of a 1T field.

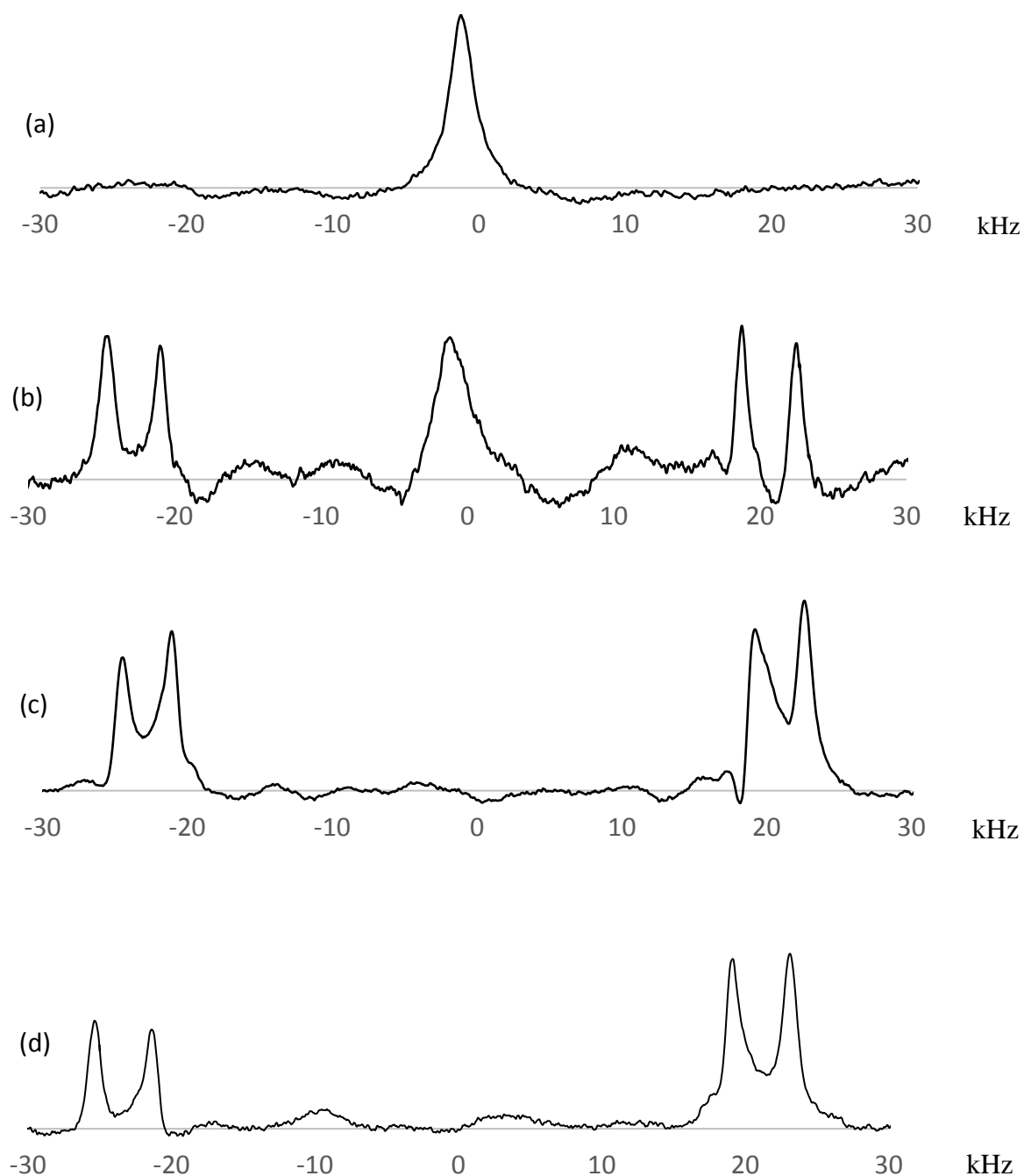


Figure 10. The deuterium NMR spectra of the spin probe CB7CB-d<sub>4</sub> doped (2.8wt %) in an equimolar mixture of 2O.3.O2 and 2O.5.O2 mixture in (a) the I phase at 91°C, (b) the biphasic I+N<sub>TB</sub> phase at 89°C, (c) the N<sub>TB</sub> phase at 88°C and (d) the N<sub>TB</sub> phase at 85°C. The sample was contained in a short NMR tube orthogonal to the field, it was degassed and the tube sealed.

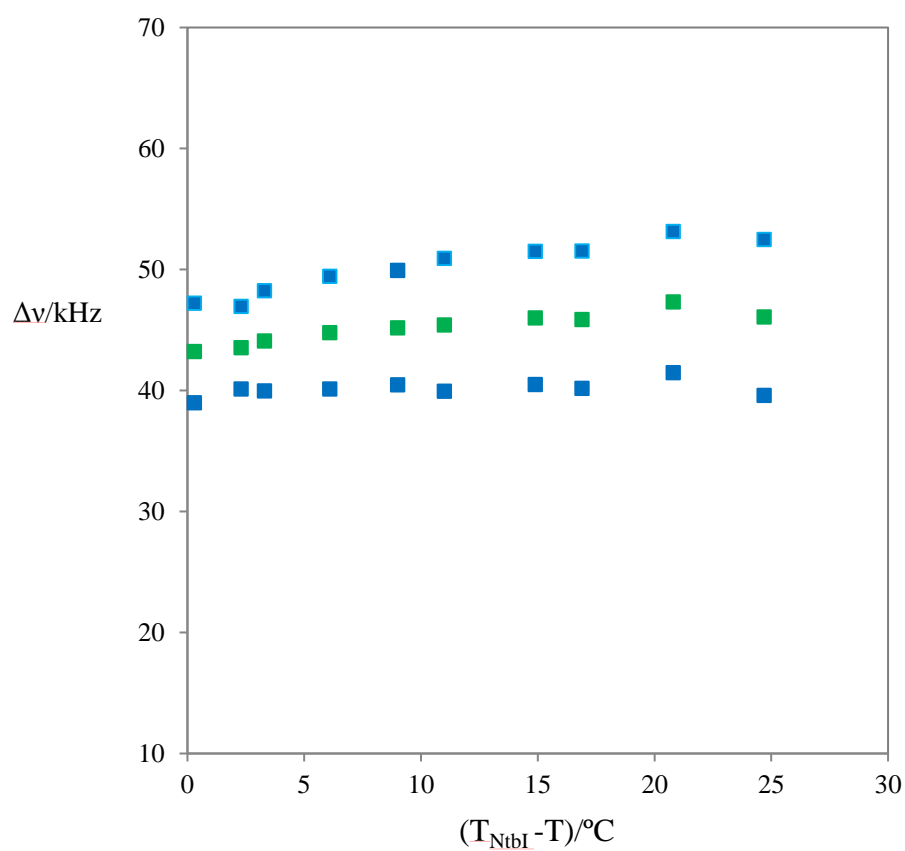


Figure 11. The dependence, on the shifted temperature ( $T_{NtbI} - T$ ), of the quadrupolar splittings,  $\Delta\nu$ , for 2.8wt % of the spin probe CB7CB- $d_4$  in the equimolar mixture of 2O.3.O2 and 2O.5.O2. Here ■ denotes the two prochiral quadrupolar splittings in the  $N_{TB}$  phase and ■ the mean of these two splittings.